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Photophysics of polymer-wrapped single-walled carbon nanotubes

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Abstract. Single-walled carbon nanotubes (SWNTs) are successfully dispersed in two conjugated polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and poly[2-methoxy-5- (2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEHPPV) solutions. Steady-state and time-resolved photoluminescence spectroscopy in the near-infrared and visible spectral regions are used to study the interaction of the dispersed carbon nanotube and the wrapped polymer in the nano-hybrids. The SWNTs infrared emission is the signatures of the separation of single semiconducting tubes, the lifetime of the photoluminescence of these tubes is bi-exponential with the first component varying from 6 ps (in MEHPPV wrapped SWNTs) to 14 ps (in PFO wrapped SWNTs), while the second component of the decay for all samples is in the range of 30−40 ps, revealing the intrinsic lifetime of the SWNTs. The study of the photoluminescence of the nano-hybrids in the visible spectral range shows, in the case of the PFO, a relatively strong quenching, the photoluminescence lifetime for the hybrid is more than 100 ps shorter than the one of the pristine polyfluorene solution. For the MEHPPV-SWNT hybrid an opposite behavior is revealed with the photoluminescence lifetime surprisingly longer than the polymer solution. The possible mechanism for the interaction of the two conjugated polymers and the SWNTs is discussed in terms of their electronic band structure.

PACS. 78.67.Ch Nanotubes – 81.07.-b Nanoscale materials and structures: fabrication and characterization

1 Introduction

Single-walled carbon nanotubes (SWNTs) are hollow cylinders composed by carbon atoms that have remained at the forefront of nanotechnology research for two decades [1–3]. Individual SWNTs exhibit robustness and high thermal and chemical stability but their outstanding physical properties are strongly dependent on their diameter and chirality that are determined by the wrapping direction of the graphene sheet. One third of the carbon nanotubes produced with the standard synthetic procedures is metallic while the rest are semiconducting [4,5].

In SWNTs as in all one-dimensional systems the density of states (DOS) displays sharp peaks called van Hove singularities, the optical transitions between these singularities are allowed and determine the photophysical properties of the carbon nanotubes. Due to the strong tendency of carbon nanotubes to aggregate and to form bundles the first optical studies had a limited success in disclosing the intrinsic properties of these one-dimensional objects. The optical absorbance exhibited inhomogeneous broadening due to the mixing of electronic band of different SWNTs composing the bundles. Moreover, no or very weak fluorescence could be observed from the bundles containing metallic SWNTs, which provide efficient non-radiative pathways for the photoexcitations. In 2002, O'Connell et al. [6], succeeded to disperse SWNTs by using as surfactant sodium dodecyl sulfonate (SDS), this first experiment opened the way for deep photophysical studies aimed to the understanding of the fundamental properties of SWNTs. Later on, many materials have been used for the dispersion of carbon nanotubes including surfactants like sodium dodecylbenzene sulfonate (SDBS) [7], sodium salts of deoxycholic acid (DOC) [8], sodium cholate, single-stranded DNA [9], etc. Several methods including electrophoretic separation, chromatography and density gradient ultracentrifugation were explored to obtain selective dispersion [10–12]. Recently, π-conjugated polymers have been proved to be excellent candidates for the dispersion and selective separation of semiconducting single-walled carbon nanotubes [13]. Among the polymers used for this purpose polyfluorene and its derivates showed unique selectivity [13]. Moreover, new photophysical properties are expected for these one dimensional polymer-SWNTs hybrid systems that might have potential for future nanophotonics and nanophotovoltaic device applications.

In this work we report about the photophysical properties of the polymer-SWNTs hybrids with emission both in the visible (from the polymer) and in the near infrared

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(from the SWNTs) spectral range. A narrow diameter distribution and a low content of metallic tubes are obtained starting from a Comocat SWNTs mixture, thanks to the interaction with the polymer chains. After removal of the isolated polymer, the dispersion was studied by means of steady-state and time-resolved photoluminescence spectroscopy. The intrinsic lifetime of SWNTs is found to be in the range of 30−40 ps. The photoluminescence of the wrapped PFO showed faster decay (268 ps) compared to the one of the polymer solution (380 ps). The origin of the quenching of the PL intensity is discussed in term of Förster resonant energy transfer. At the opposite than in the PFO case the photoluminescence decay of the wrapped MEHPPV is slower than the one of the pristine solution indicating a different mechanism for the interaction of this polymer with the SWNTs.

2 Experimental section

The polymers poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO) and poly[2-methoxy-5- (2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEHPPV) were purchased from Sigma Aldrich. The Comocat SWNTs were purchased from Southwest Nanotech. All the materials were used as received. The carbon nanotube powders were dispersed in the polymer solution in the ratio of 1 mg SWNTs: 3 mg polymer in 6 ml toluene and sonicated for about 6 h in an ultrasonic bath. After sonication the solution was centrifuged at 4000 rpm for 5 min. The supernatant solution was taken for the measurements. To wash out the isolated polymer, the solution was filtered through a 100 nm Teflon filter and rinse with toluene several times till no photoluminescence emission (PL) was detected from the filtrate [14]. Finally, the filter was steeped in toluene and mildly sonicated for about 10 min, yielding to a SWNTs-enriched solution with minimal polymer residue. For the steady-state and time resolved photoluminescence measurements, the solutions were excited by a 150 fs pulse Kerr mode locked Ti-sapphire laser, at 760 nm or doubled at 380 nm. The steady-state PL of the SWNTs was measured with an InGaAs detector and the one of the polymer with a Si-CCD detector. The time-resolved PL of the hybrid was recorded by two Hamamatsu streak cameras working in synchroscan mode, one with a photocathode sensitive in the visible and the other in the near infrared spectral range. All the measurements were performed with the samples at room temperature.

3 Results and discussion

The absorbance and photoluminescence spectra of the SWNTs dispersion in the two polymer solutions are shown in Figures 1a, 1b and 1c, 1d, respectively. The characteristic absorption spectra in the wavelength range from 500 to 1600 nm corresponds to the first and second van Hove transitions (E_{11}, E_{22}) of semiconducting nanotubes. Both the absorption and the PL spectra of SWNTs dispersed with PFO and MEHPPV appear to be red-shifted of 12−19 nm compared to the spectra measured for samples in aqueous-based surfactant dispersions. Such a red shift is attributed to the different dielectric constant of the environment [15]. The PL spectrum of the polymer-wrapped SWNTs shows good matching with the absorption spectra, with a Stokes shift of less than 6 meV. In the PFO dispersion (Fig. 1a), the low absorbance background and the narrow absorption peaks matching the E_{11} transition of semiconducting SWNTs demonstrate that the sample is composed by individual SWNTs and eventually of very small semiconducting bundles. From the absorption spectrum the solution contains mainly 5 kinds of small nanotubes with high chirality, namely the (7,5), (7,6), (8,6), (8,7), (9,7). The high selectivity of the PFO dispersion appears to be due to the strong interaction between the polymer chain and the SWNTs [16]. In the case of the SWNTs wrapped with MEHPPV (Fig. 1b) the absorbance background intensity is much higher than in the PFO case and the spectrum emerges as less-resolved. Moreover, the PL intensity of the SWNTs wrapped with MEHPPV (Fig. 1d) is more than one order of magnitude lower than the one of the hybrids prepared with PFO (Fig. 1c). Both data indicate the presence in the MEHPPV dispersion of residual nanotubes bundles. This is also consistent with the faster decay of the PL for this sample as is discussed in detail below. Unlike the high selectivity shown by the PFO dispersion, the MEHPPV dispersion shows limited selectivity. The dissimilar affinity of the two polymers for the SWNTs is to be attributed to the different structure and chain conformation in solution [17].

The photoluminescence decay of the (7,5) SWNTs excited at 760 nm is shown in Figure 2 in blue and red for the PFO and the MEHPPV dispersion, respectively. The decay in both cases can be accurately fitted with a bi-exponential function. In the PFO dispersion, the decay is composed by a fast component with time constant of ∼14 ps and a slow component of ∼35 ps. For the MEHPPV-based dispersion the first component has a decay of ∼6 ps and the second has, as in the case of the PFO dispersion, a decay time of ∼32 ps. The faster decay time observed in the MEHPPV dispersion is attributed to the energy transfer between adjacent tubes located in small bundles [18].

Previously, several authors reporting measurements performed with techniques such as pump-probe and time resolved PL have shown similar lifetimes for SWNTs [19–21]. The first fast component of the decay can be attributed to the high non-radiative losses of the photoexcited exciton population through several pathways. One of the most relevant of these pathways is towards the intrinsic 'dark' excitonic states that are supposed to be located between few to hundreds of milli-electron-volts below the 'bright' exciton state [22]. Others quenching sites can be identified in the wall defects and in the tube ends, in the case of the bundles, new opportunities for non-radiative pathways are opened thanks to the inter-tube interaction.

The long decay component of about 35 ps represents the intrinsic lifetime of SWNTs. In the literature values in

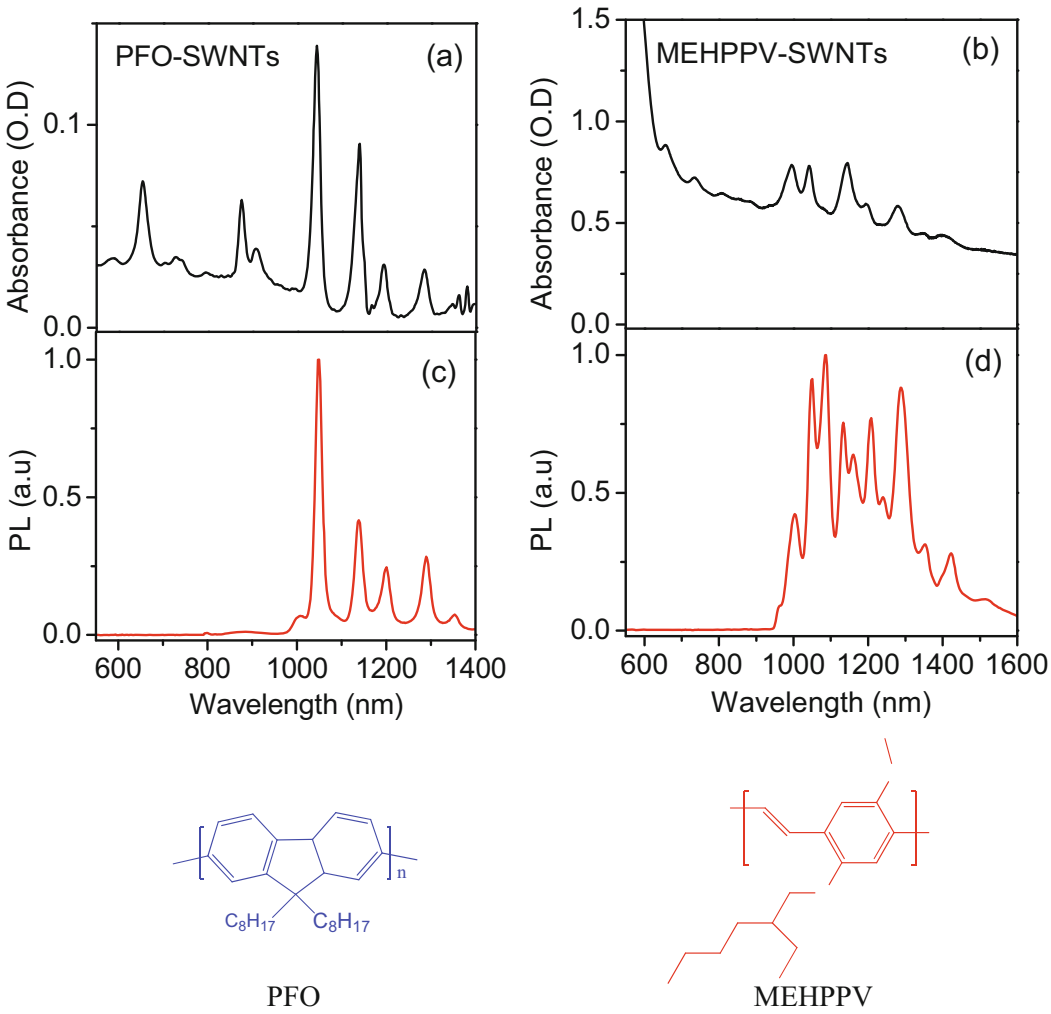

Fig. 1. (Color online) Absorbance (black curves) and photoluminescence (red curves) spectra of SWNTs dispersed in different polymer/toluene solutions: (a) absorbance of the PFO-wrapped SWNTs (b) absorbance of the MEHPPV-wrapped SWNTs. (c) PL spectrum of the PFO-wrapped SWNTs (d) PL spectrum of the MEHPPV-wrapped SWNTs. The PL spectra are normalized at their maximum intensity. The chemical structures with the respective names of the polymer are shown at the bottom.

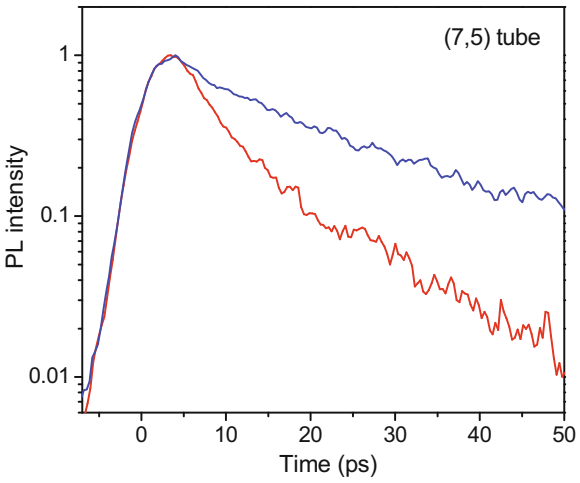

Fig. 2. (Color online) PL decay of the (7,5) SWNT dispersed with PFO (blue curve) and with MEHPPV (red curve). The intensity is normalized at $t = 0$ and the samples were excited at 760 nm.

the range between 20 ps to 200 ps have been reported by using different kinds of nanotubes and separation methods [23,24]. In order to demonstrate the universal lifetime of the Comocat SWNTs used in our experiments, different dispersions in aqueous solutions were produced by following the same procedure reported previously and using as surfactants SDS, SDBS, DOC and single-stranded DNA. The measured lifetime of the SWNTs in all the cases is in the range of 30−40 ps, consistently with our measurements on polymer-wrapped tubes and with previous reports for small diameter SWNTs [25]. Other kinds of SWNTs like the Hipco (high pressure CO conversion) from Carbon Nanotechnologies, Inc or PLV (Pulsed Laser Vaporization) ones from Chengdu Organic Chemicals Co. Ltd were also studied. Noteworthy, the PL decay of similar tubes synthesized with these methods and the Comocat are different. Such broad range of lifetimes points out to the fact that there are extrinsic factors such as impurities and defects that determine the exciton decay. We can safely exclude in our case the effect of the sample

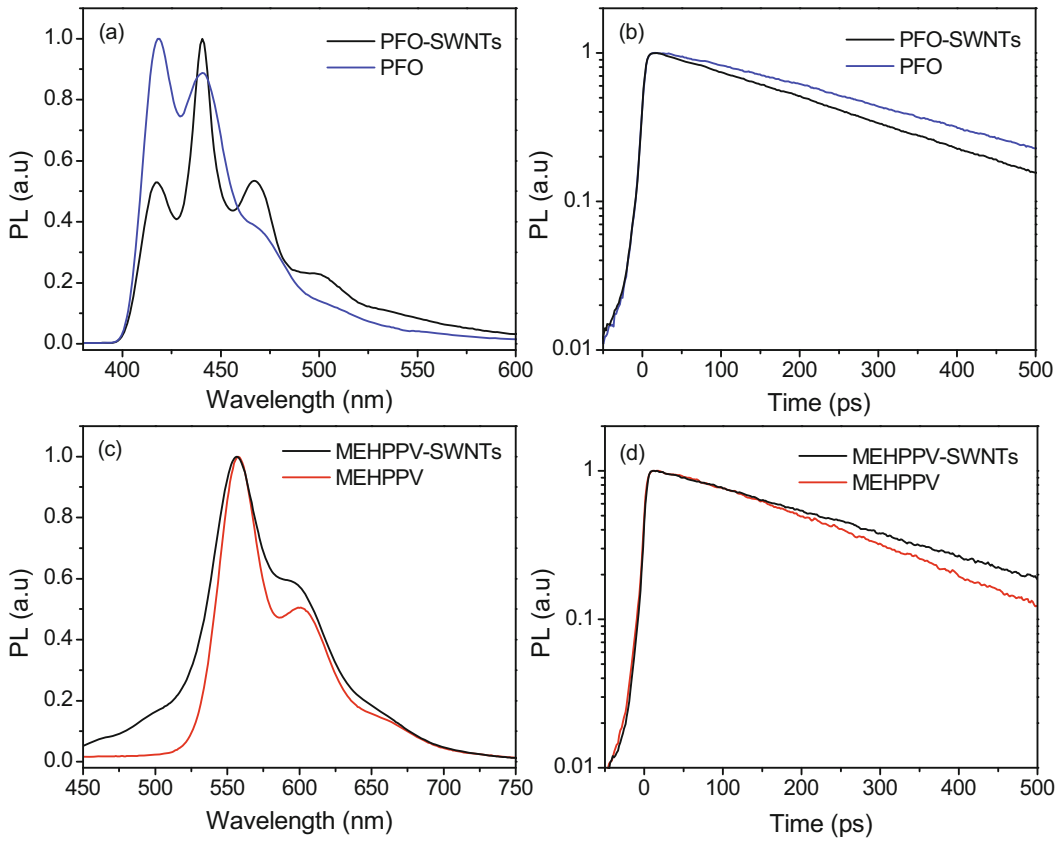

Fig. 3. (Color online) Steady-state and time-resolved PL of the polymer wrapped around the SWNTs and the polymer solution: (a) PL spectra of the PFO solution and of the PFO-SWNTs hybrid. (b) PL decay of PFO and of the PFO-SWNTs hybrid at 450 nm. (c) PL spectra of the MEHPPV solution and of the MEHPPV-SWNTs hybrid. (d) PL decay of MEHPPV and of the MEHPPV-SWNTs hybrid at 630 nm.

preparation (in particular the sonication) because all the samples have been treated in the same way.

Figure 3 shows the steady state and time-resolved photoluminescence of the PFO and MEHPPV interacting with the SWNTs after removal of the residual polymer from the solution. The PFO wrapped around the SWNTs shows better resolved PL spectrum than that of the polymer solution (Fig. 3a). The appearance of this sharp vibronic progression can be ascribed to the rigid conformation assumed by the polymer chain around the carbon nanotubes. Recent molecular dynamics simulations indicate that two conformations are possible for the PFO chains in this composite [17,26], one in which the side chains are wrapped around the tube, the other with the polymer backbone attached to the carbon nanotube walls through $\pi-\pi$ interaction. In both cases, the carbon nanotube is tightly caged by the polymer chain, while only the second configuration agrees with the experimental finding of a more resolved photoluminescence spectrum. The photoluminescence decay of the PFO wrapped around the SWNTs shows a mono-exponential behavior with a lifetime $\tau = 268$ ps, that is more than 100 ps shorter than that of the polymer solution ($\tau = 380$ ps) (Fig. 3b). This result evidences the interaction of the two components of the nano-hybrid and could be explained by an energy transfer or a charge transfer from the polymer to the carbon nanotube. Between these two possible mechanisms the energy transfer from the excited donor to the acceptor by non radiative coupling between the dipoles appears more possible [27]. The conditions necessary to allow the energy transfer are (i) the overlap between the emission spectrum of the donor and the absorbance of the acceptor, (ii) a short distance between the donor and the acceptor and (iii) the transition dipoles oriented in the same direction. Considering that the Fermi level of the (7,5) SWNTs is around 4.7 eV [28], the low energy tail of the fluorescence emission of PFO and the higher absorption transition of the nanotube are at the same energy and the heterojunction between PFO and the (7,5) tube results to be of type 1. Moreover, the distance between the wrapped polymer and the nanotube can be easily assumed to be less than 10 nm.

In Figure 3c are reported the PL spectra of the MEHPPV-SWNTs hybrid and of MEHPPV in solution. The PL spectra of the MEHPPV appear to be modified by the interaction with the carbon nanotube showing a redistribution of the PL intensity and a new emission shoulder in the high energy portion of the spectra. The PL decay of the nano-hybrid (shown in Fig. 3d) is surprisingly slower

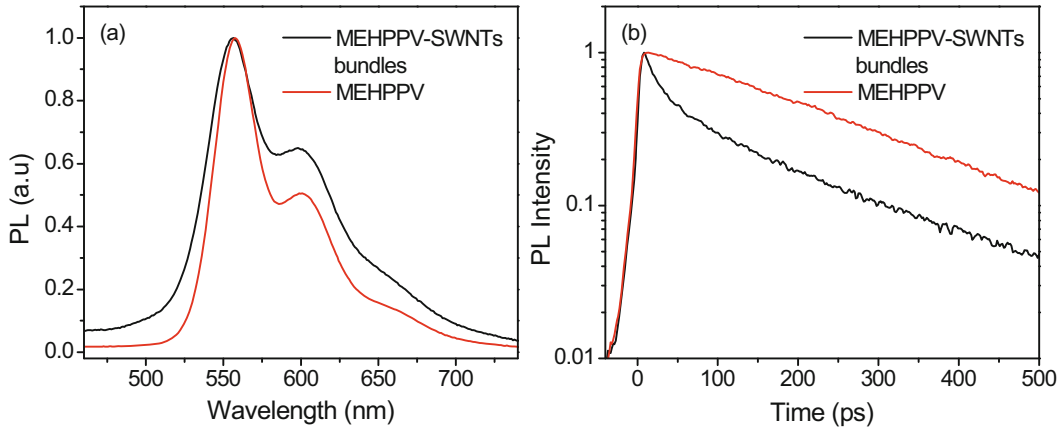

Fig. 4. (Color online) Steady-state and time-resolved PL of the MEHPPV wrapped around SWNTs bundles: (a) PL spectra of the MEHPPV wrapped around SWNTs bundles and MEHPPV solution. (b) PL decay of MEHPPV-SWNTs bundles and MEHPPV solution.

than that of polymer in solution with a mono-exponential lifetime of 293 ps. Such a long lifetime can be rationalized as coming from a more delocalized excited state in the nano-hybrid than in the polymer chain in solution. Although the band offset between the highest occupied molecular orbital (HOMO) of MEHPPV and the valence band of the semiconducting carbon nanotubes [29] is such to be considered a type 2 heterojunction and consequently to favor the electron transfer from the photoexcited polymer to the SWNTs the experimental results demonstrate that this is not happening, at least for the (7,5) nanotubes.

Previous works showed that by adding SWNTs into an MEHPPV-based organic light-emitting diode the device electroluminescence resulted to be strongly quenched [30]. In order to explain these results that seem to be in contradiction with our experiments on the MEHPPV-wrapped SWNTs, we have analyzed the sediment resulting from the centrifugation. The sediment of the polymer-SWNT solution, at the opposite of the supernatant, consists of polymer-wrapped big carbon nanotubes bundles and various kind of heavy impurities. The steady-state and time-resolved PL of the polymer present in this sample are reported in Figures 4a and 4b, respectively. The photoluminescence spectra of the polymer-bundles are similar to the one of the polymer solution with a weak intensity redistribution that can be eventually attributed to a different chain conformation. The PL decay of the polymer-bundles shows a bi-exponential behavior with a fast component of 21 ps and a slow one of 240 ps, the last approaches the lifetime of the pristine polymer that is about 275 ps. Since the big bundles of carbon nanotubes have a very high chance to contain metallic tubes, the system can be safely regarded as a polymer-metallic wire composite. On the light of this last result we speculate that the PL quenching of MEHPPV by SWNTs reported in previous works [31] is mainly due to the presence of metallic tubes. It is important to underline that the availability of samples enriched of semiconducting tubes, as the one here reported, allows shedding light not only on the properties of carbon nanotubes but also on their interaction with others systems.

4 Conclusion

Polymer-wrapped single-walled carbon nanotubes were prepared with two different conjugated polymers showing different affinity for Comocat tubes. These hybrid systems were used to obtain a sample enriched of semiconducting SWNTs and measure their intrinsic lifetime that is found to be in the range of 30−40 ps. In the SWNTs dispersion with PFO, the fluorescence of the polymer is quenched due to the energy transfer towards the nanotube. Conversely, in the case of MEHPPV the PL decay became slower indicating the formation of a more delocalized excited state in the composite. The quenching of the MEHPPV photoluminescence is observed when the polymer is in contact with bundles of SWNTs owing to the presence of metallic nanotubes.

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